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Effects of alkyl group and temperature on the interactions between furfural and alcohol: Insight from density and sound velocity studies



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ABSTRACT

In this work, the study of the interactions between furfural and alcohol mixtures are discussed through insight from density and sound velocity measurements. The density (ρ) and sound velocity (u) of furfural, alcohols such as ethanol, 1-butanol, 2-butanol, and their binary systems {furfural (x_1)+ethanol or 1-butanol or 2-butanol (x_2)} were measured at (283.15, 293.15, 303.15, and 313.15) K and at $p = 1 \times 10^5$ Pa. The sound velocity data were tested by using sound velocity mixing rules to calculate the sound velocity of the binary mixture from pure component data. The derived properties such as excess molar volumes, $V_{\rm m}^{\rm E}$, isentropic compressibility, κ_s , and deviation in isentropic compressibility, $\Delta \kappa_s$, were also calculated. The Redlich–Kister polynomial equation was used to fit the excess/deviation properties. The semi-empirical calculation with the help of HyperChem 7 shows that furfural interacts with the alcohol through the H-bonding.

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1. Introduction

Climate change and the depletion of fossil fuels form the driving force behind the utilization of alternative and renewable energy sources [1–5]. Among various energy alternatives, biofuels, hydrogen, natural gas and syngas (synthesis gas) arise as the four strategically important sustainable fuel sources in the future. Recent studies have shown that between these four, biofuels are promising fuel source of the future due to their renewability, biodegradability, and generation of acceptable quality exhaust gases [6]. They can be produced domestically from a wide variety of biomass sources [7,8].

Derived from lignocellulose biomass, furfural is regaining attention as a bio-based alternative for the production of several products from antacids to fertilizers, plastics, and paints. Recently, it was identified as one of the most promising chemicals for sustainable production of fuels and chemicals in 21st century [9]. It is the natural dehydration product of five-carbon sugars (arabinose and xylose) that are derived from hemicelluloses biomass [10].

The knowledge of thermophysical (density, sound velocity, refractive index and viscosity) and thermodynamic (heat capacity, Gibbs free energy, excess molar volume and excess molar

enthalpy) properties [11,12] allow for the development of new correlations and/or predictive models. These properties are also important to investigate the intermolecular interactions that can occur in liquid mixtures, especially where hydrogen bonding occurs [13–16]. In this regard, the present work is a continuation of our systematic studies on thermodynamic and thermophysical properties of binary mixtures containing solvents derived from biomass [17–23].

In this paper, we report the densities, and sound velocities for the binary systems {furfural (x_1) +ethanol, or 1-butanol, or 2-butanol (x_2) } over the entire composition range and at (283.15, 293.15, 303.15 and 313.15)K and at $p = 1 \times 10^5$ Pa. These results were used to calculate the excess molar volumes, isentropic compressibility, and deviation in isentropic compressibility, respectively, over the entire composition range and at each temperature. The Redlich–Kister polynomial equation was fitted to the excess molar volume and deviation in isentropic compressibility. Four sound velocity mixing rules were applied to the experimental data. The open literature shows that there are no data available for the binary systems investigated.

2. Experimental

2.1. Chemicals

The chemical substances were supplied by Aldrich Chem. (Milwaukee, WI, USA). The purities of all chemicals, tested by GC

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(gas chromatography), were better than 0.99 (mass fraction). The source, purification method and purity of all chemicals used in this study are given in Table 1. The purities of the chemicals were also checked by comparing the experimental density and sound velocity values of the pure chemicals at various temperatures with those reported in literature [24–35]. These results are given in Table 2. No further purification of these chemicals was required.

2.2. Apparatus and procedure

Binary mixtures were prepared by mass, using an OHAUS analytical balance with a precision of ± 0.1 kg. The estimated error in the mole fraction was 0.0005. The details of the experimental procedure can be found elsewhere [36]. A binary test system (diethyl carbonate + ethanol) [29] was previously measured [21,22] to validate the experimental technique. The calculated excess molar volumes, isentropic compressibility, deviation in isentropic compressibility were compared to literature values. The difference between the experimental and literature excess molar volumes, isentropic compressibility, and deviation in isentropic compressibility was within the experimental error.

Density and sound velocity for pure components and binary mixtures were measured using a digital vibrating-tube densimeter and sound velocity analyzer (Anton Paar DSA 5000M) with an accuracy of ± 0.02 K in temperature. The estimated errors in density and sound velocity were less than $\pm 0.01 \text{ kg m}^{-3}$ and $\pm 0.5 \text{ m s}^{-1}$, respectively. The instrument can measure simultaneously density in the range from 0 to 3×10^3 kg m⁻³ and sound velocity from 1000 to $2000 \,\mathrm{m\,s^{-1}}$ in a temperature range from 273.15 to 343.15 K with pressure variation from 0 to 0.3×10^5 Pa. The sound velocity is measured using a propagation time technique [37]. The sample is sandwiched between two piezoelectric ultrasound transducers. One transducer emits sound waves through the sample-filled cavity (frequency around 3 MHz) and the second transducer receives those waves. Thus, the sound velocity is obtained by dividing the known distance between transmitter and receiver by the measured propagation time of the sound waves [37]. The estimated error in excess molar volume, isentropic compressibility, deviation in isentropic compressibility is $\pm 0.003 \times 10^3 \text{ m}^3 \text{ mol}^{-1}$, $\pm 1 \times 10^{12} \text{ Pa}^{-1}$ and $\pm 0.6 \times 10^{12}$ Pa⁻¹, respectively.

The structures of furfural and alcohol were optimized based on molecular mechanics and semi-empirical calculations using the HyperChem 7 molecular visualization and simulation program. Initial molecular geometry of furfural and the alcohols viz. ethanol, 1-butanol and 2-butanol were optimized with the AM1 semiempirical calculations. The optimized molecules of furfural and alcohols were placed on top of each other symmetrically with an inter planar distance of between 2.3 and 3.0 Å and the angle of between 50 and 70°. Further, the geometries were optimized using the molecular mechanics (MM+force field), AM1 semi-empirical calculations, and the Polak–Ribiere routine with rms gradient of 0.01 [38,39]. Hydrogen bonds were displayed using HyperChem 7 "show hydrogen bonds" and "recomputed hydrogen bond" options.

Table 1

Pure component specifications: suppliers, CAS number, specified purity and GC purity.

Chemical name	Supplier	CAS No.	Mass fraction purity	
			Initial	GC analysis
Furfural	Aldrich	98-01-1	≥0.99	>0.99
Ethanol	Aldrich	64-17-5	≥ 0.99	>0.99
1-Butanol	Aldrich	71-36-3	≥ 0.99	>0.99
2-Butanol	Aldrich	78-92-2	≥ 0.99	>0.99

Table 2

Comparison of experimental density, ρ , and sound velocity, u, of the pure component with the corresponding literature values at (283.15, 293.15, 303.15 and 313.15)K and at $p = 1 \times 10^5$ Pa.

Component	Т (К)	ho (kg m ⁻³)		$\frac{u}{(m s^{-1})}$	
		Exp.	Lit.	Exp.	Lit.
Furfural	283.15	1169.93	-	1495.4	-
	293.15	1159.33	1160 [24]	1458.8	1460 [33]
	303.15	1148.69	1151 [24]	1422.5	-
			1149.766 [25]		
	313.15	1138.01	-	1386.5	-
Ethanol	283.15	798.51	797.89 [26]	1197.3	-
	293.15	789.99	789.50 [27]	1162.5	1160 [29]
			789.40 [28]		1160.3 [34]
	202.15	701 20	789.30 [29]	1120.2	1120 [20]
	303.15	/81.38	780.7 [29]	1128.3	1126 [29]
	212.15	772 64	781.8 [30]	1004.0	1126.2 [34]
	313.15	//2.64	772.1 [29]	1094.6	1093 [29]
			773.4 [20]		1092.7 [34]
1-Butanol	283 15	81721	81712 [31]	12914	1292 45 [35]
i butunoi	293.15	809.65	809 5 [29]	1257.5	1257 [29]
	200110	000100	00010 [20]	120710	1257.66 [35]
	303.15	802.00	801.8 [28]	1223.6	1224 [29]
			803.7 [32]		1223.55 [35]
	313.15	794.21	794.1 [29]	1190.2	1190 [29]
			796.7 [32]		1190.28 [35]
2-Butanol	283.15	815.39	814.52 [31]	1268.4	-
	293.15	807.34	806.7 [29]	1232.4	1230 [29]
	303.15	798.99	798.4 [29]	1196.1	1195 [29]
			798.8 [32]		
	313.15	790.28	789.5 [29]	1159.5	1157 [29]
			791.1 [32]		

Standard uncertainties u are $u(T) = \pm 0.02$ K, $u(p) = \pm 4 \times 10^4$ Pa and the combined expanded uncertainty U_c in density and sound velocity measurements were less than $U_c(\rho) = \pm 0.01$ kg m⁻³ and $U_c(u) = \pm 0.5$ m s⁻¹, respectively (0.95 level of confidence).

3. Results and discussion

3.1. Thermophysical properties

3.1.1. Density

The density, ρ , was measured at (283.15, 293.15, 303.15 and 313.15)K, and at $p = 1 \times 10^5$ Pa for the {furfural (x_1)+ethanol, or 1-butanol, or 2-butanol (x_2)} systems and are given in Table 3. The plots of density versus concentration at investigated temperatures are given in Fig. 1S((a)–(c)). From Fig. 1S ((a)–(c)), it can be seen that the ρ values decreases linearly with an increase in temperature and increases with an increase in the concentration of furfural for all binary systems.

3.1.2. Sound velocity

Sound velocity is also an important property which describes the solvent–solvent, solute–solvent and solute–solute interactions in the mixture [40]. In this regards, the sound velocity data, *u*, were also measured at (283.15, 293.15, 303.15 and 313.15) K, and at $p = 1 \times 10^5$ Pa for {furfural (x_1) + ethanol, or 1-butanol, or 2-butanol (x_2)} systems and are given in Tables 3. The plots of sound velocity versus concentration, at investigated temperatures, are given in Fig. 2S((a)–(c)). From this Fig. 2S((a)–(c)), it can be seen that the *u* values also decreases linearly with an increase in temperature and increases with an increase in the concentration of furfural for all binary systems.

Further, the sound velocity data were tested using sound velocity mixing rules to calculate the sound velocity of the binary mixture from pure component data. The mixing rules used and Download English Version:

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